

## HOLLANDITE AND LITHIOPHORITE IN BURROWS OF LATE CRETACEOUS AGE, NORTHEASTERN SOUTH CAROLINA

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### ABSTRACT

Hollandite  $BaMn_8O_{16}$  and lithiophorite  $(Al,Li)MnO_2(OH)_2$  constitute the cement of burrows of Santonian Age in northeastern South Carolina. The burrows were formed at the interface between gravels of the Upper Cretaceous Middendorf Formation and the underlying saprolite of felsic metavolcanic rocks of the Piedmont physiographic province. The hollandite and lithiophorite are considered to be primary minerals formed while the burrowing organisms inhabited these tubes. The absence of these minerals in ironstone in the saprolite and at the saprolite-Middendorf contact supports this conclusion.

**Keywords:** hollandite, lithiophorite, burrows, Upper Cretaceous.

### SOMMAIRE

La hollandite  $BaMn_8O_{16}$  et la lithiophorite  $(Al,Li)MnO_2(OH)_2$  constituent le ciment de tubules d'âge santonien dans le nord-est de la Caroline du sud. Ces tubules se présentent au contact des graviers de la formation Middendorf (Crétacé supérieur) avec la saprolite sous-jacente formée aux dépens des roches métavolcaniques felsiques de la province physiographique du Piedmont. Hollandite et lithiophorite sont à considérer ici comme minéraux primaires, datant de l'occupation de ces tubules par les organismes fouisseurs, conclusion qu'étaye leur absence des sédiments ferrugineux de la saprolite et de la zone du contact Middendorf-saprolite.

(Traduit par la Rédaction)

**Mots-clés:** hollandite, lithiophorite, tubules, Crétacé supérieur.

### INTRODUCTION

During field reconnaissance of basal Coastal Plain sediments near the Fall Line in northeastern South Carolina, five burrows were found at the interface between the Coastal Plain sediments and the underlying weathered metavolcanic rocks of the Piedmont province. Scanning electron micrographs (SEM) and powder-diffraction patterns of sediment from two burrows reveal the presence of major amounts of hol-

landite and lesser amounts of lithiophorite as constituents of the cemented burrow filling. This article will describe the geological setting in which the hollandite and lithiophorite occur and present a hypothesis regarding their origin.

### GEOLOGICAL SETTING

The burrows discussed herein were found in a borrow pit on the north side of Route 348, 9.6 km northwest of Cheraw, South Carolina (Fig. 1). At this locality, the Middendorf Formation of Santonian age (R. A. Christopher, verbal comm. 1979) rests unconformably on saprolite derived from felsic metavolcanic rocks of the Carolina slate belt of the Piedmont (Fig. 2). There, the Middendorf is an interbedded sequence of cross-bedded feldspathic sand and gravel and laminated kaolinitic clay. Although no microflora or microfauna are present in the Middendorf beds at this locality, a marine or marginal-marine origin for the burrows is suggested (1) by the reported presence of foraminifera in Middendorf beds in an outcrop less than 10 km to the southeast (Siple *et al.* 1956), and (2) by the presence of the burrows discussed here, at the contact between the gravel of the Middendorf Formation and the underlying saprolite.

The saprolite is weathered from metavolcanic rocks of early Paleozoic age, and ranges in thickness from 2 to 5 m. Results of an X-ray-fluorescence analysis of the saprolite are given in Table 1.

Burrows observed at this locality extend from the Middendorf-saprolite contact into the saprolite and are filled with sand of the Middendorf that has been cemented by manganese oxide into thin- to thick-walled tubes (Fig. 3). The burrows are brown, coherent, cylindrical, noded, straight and nonbranching and do not have striae or linings (Fig. 4).

### MINERALOGY OF BURROWS

SEM photomicrographs indicate the presence

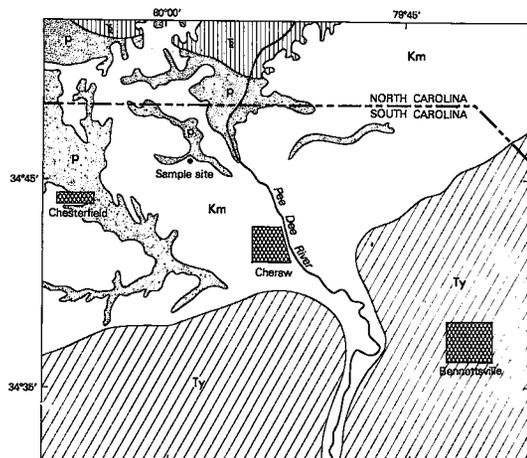


FIG. 1. Index map showing location of outcrop with burrows at the contact between sands of the Middendorf Formation of Late Cretaceous age (Km) and saprolite of the felsic metavolcanic rocks of the Carolina slate belt of the Piedmont province. Triassic rocks are denoted by Tr, the Yorktown Formation (Pliocene) by Ty.

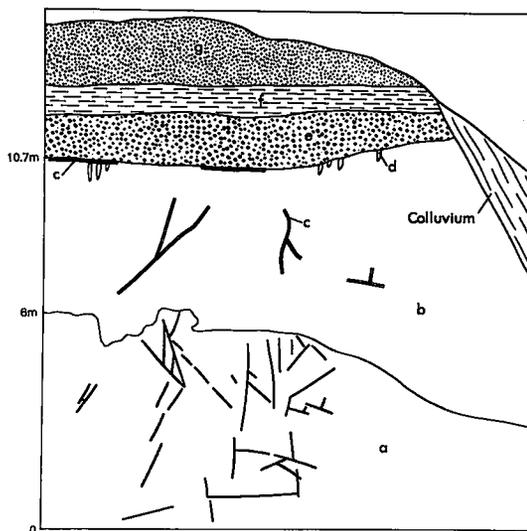


FIG. 2. A schematic drawing of the outcrop showing the irregular contact between the saprolite (b) and the highly jointed felsic metavolcanic rocks (a). Lenses of ironstone (c) follow the joints in the saprolite and are discontinuous along the contact between the saprolite (b) and the overlying sediments of the Upper Cretaceous Middendorf Formation. Burrows (d) are within the saprolite and have linings of Fe and Mn oxides consisting of the minerals hollandite and lithiophorite. The Middendorf Formation (Km), here composed of cross-bedded gravels (e), sands (g) and interbeds of laminated clay (f), is considered to be of marine origin.

TABLE 1. X-RAY-FLUORESCENCE ANALYSIS\*

	Saprolite LB-190	Burrow 79WCF27	Contact ironstone 79WCF25	Ironstone 2m below contact 79WCF26
Weight percent				
Oxides:				
SiO <sub>2</sub>	69.7			
Al <sub>2</sub> O <sub>3</sub>	13.3			
Fe <sub>2</sub> O <sub>3</sub>	1.4	11.4	47.0	71.5
CaO	.28			
K <sub>2</sub> O	1.27			
TiO <sub>2</sub>	.63			
MnO	.05	17.0	.3	4.0
P <sub>2</sub> O <sub>5</sub>	.08			
TOTAL	86.7	28.4	47.3	75.5
Parts per million				
Trace elements:				
Ba	450	30,000	460	8000
Cu		500	100	
Zn		tr	100	tr
As			tr	
Pb		>200**	tr	
Rb		100	46	150
Sr		100	34	17
Zr		100	82	182
Co		500		
Y			22	10
Ce		tr		

\*Analyst, R. Johnson, U.S. Geological Survey

\*\*This concentration was higher than any of the standards available for comparison.

of hollandite and lithiophorite as the only crystalline components of the manganese oxide cement (Figs. 5, 6). Byström & Byström (1950) suggested the formula  $(Ba,K,Pb)_{2-y}(Mn,Fe)_{8-z}(O,OH)_{16}(H_2O)_u$  for hollandite. The chemical analysis of the burrow material (sample no. 79WCF27, Table 1) shows that the major elements reported by Byström & Byström (1950) are present in this sample. The energy-dispersive X-ray (EDAX) graph (Fig. 5B) shows the predominance of manganese and barium, and their relative percentages, in the sample. The X-ray-diffraction patterns of the same sample correspond to X-ray powder data for hollandite compiled by Fleischer (1964). The principal spacings in Å and their intensities, obtained using Ni-filtered Cu radiation, are 3.48 (80), 3.12 (100), 2.40 (90) and 2.14 (80).

Wadsley (1952) gave a formula of  $(Al,Li)MnO_2(OH)_2$  for lithiophorite; Fleischer & Faust (1963) noted that later analyses showed lithium to be only a minor constituent. The EDAX scan (Fig. 6B) of the crystals shown in Figure 6A indicates the presence of Mn, Al and Co in the crystal structure. X-ray powder data correspond

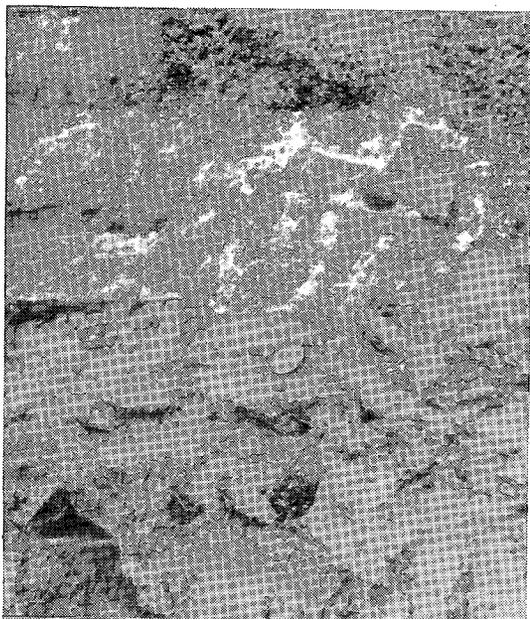


FIG. 3. Closeup of burrows at the contact between the Middendorf Formation (above), and the saprolitized felsic metavolcanic rocks. The burrows, of assumed marine origin, extend from the Middendorf-saprolite contact into the saprolite and are filled with sand of the Middendorf. Same location as Figure 2.

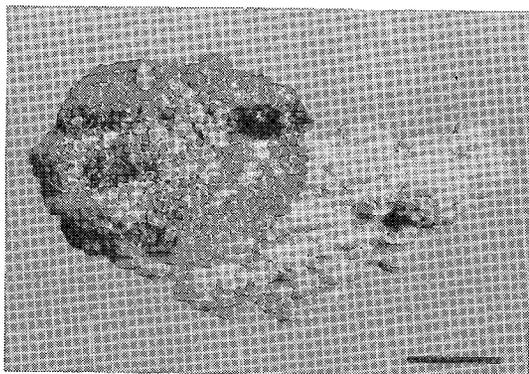


FIG. 4. Cylindrical, straight burrow with an enlarged spherical termination. Surface contains closely spaced verrucae. Burrow is filled with sand that has been cemented by manganese oxides. Included in the manganese minerals are hollandite and lithiophorite. Burrow from locality described in Figure 2. Bar = 1 cm.

to those of lithiophorite crystals compiled by Fleischer & Faust (1963). The principal spacings (in Å) and intensities for this sample are

9.50 (50), 4.71 (100), 2.36 (70) and 1.88 (70).

Hollandite was identified as the major phase in two burrows, and lithiophorite as a minor phase in one burrow. Neither hollandite nor lithiophorite was indicated from powder-diffraction patterns of the saprolite or sediment of the Middendorf Formation. Ironstone samples from the Middendorf-saprolite contact (sample no. 79WCF25, Table 1) and from 2 m below the contact in the saprolite (sample no. 79WCF26) are predominantly iron oxyhydroxide (*e.g.*, hematite and goethite) and contain low percentages of manganese. No manganese oxides were identified in the powder-diffraction patterns of the two ironstones. Barium and other trace elements are present in the ironstone samples in generally lower concentrations than in the hollandite cement of the burrows. Barium concentrations in the saprolite (LB-190, Table 1) and in the ironstones are one to two orders of magnitude lower than in the hollandite.

#### DISCUSSION

Hollandite and lithiophorite are common minerals in supergene manganese oxide deposits and have been found in many locations in the southern Appalachians (Fleischer 1964, Fleischer & Faust 1963, Pierce 1944). These minerals have not been reported, however, from sediments of the Atlantic Coastal Plain or from burrows of marine origin. The apparent absence of these manganese oxides from marine sediments of the Coastal Plain is curious in that manganese-nodule formation has been shown to be an active process at the sediment-water interface in a variety of marine settings (Glasby & Read 1976). Reduction below the interface mobilizes manganese, which diffuses upward and reprecipitates when oxidized at the sediment surface (Lynn & Bonatti 1965).

The stratigraphic relationships between burrows and substrate and the chemical data suggest that the manganese oxides formed as primary cementing minerals in the burrow linings. Several observations support this hypothesis. (1) The manganese oxides are present only within the burrows in this outcrop. The absence of manganese oxides from the enclosing sediment and the saprolite provides evidence that these minerals were not formed here by secondary supergene solutions as they were elsewhere in the southeastern United States (Pierce 1944). In addition, the supergene ironstone that formed at and below the sediment-saprolite contact shows no evidence of manganese oxide forma-

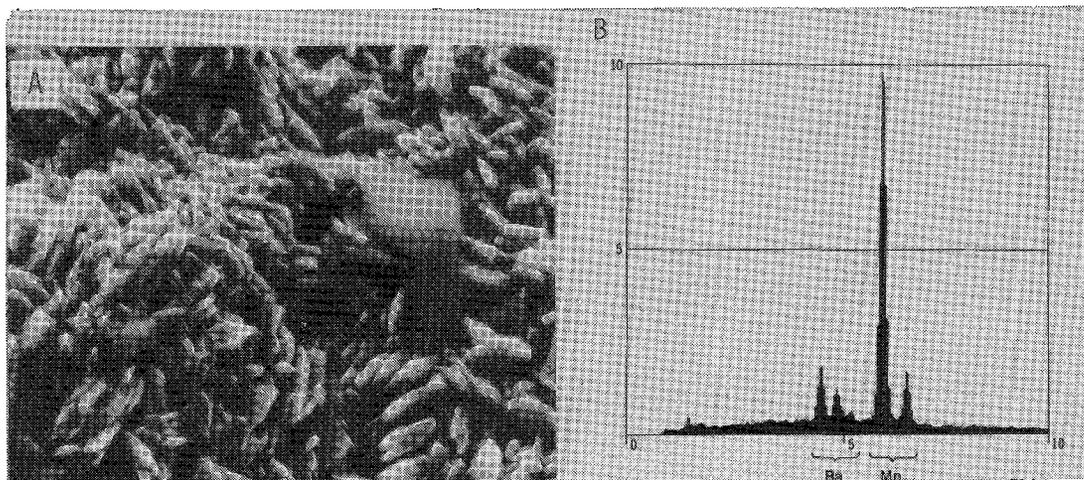


FIG. 5. (a) SEM photograph of hollandite crystals (2000x). (b) EDAX scan of hollandite crystal showing Mn and Ba peaks.

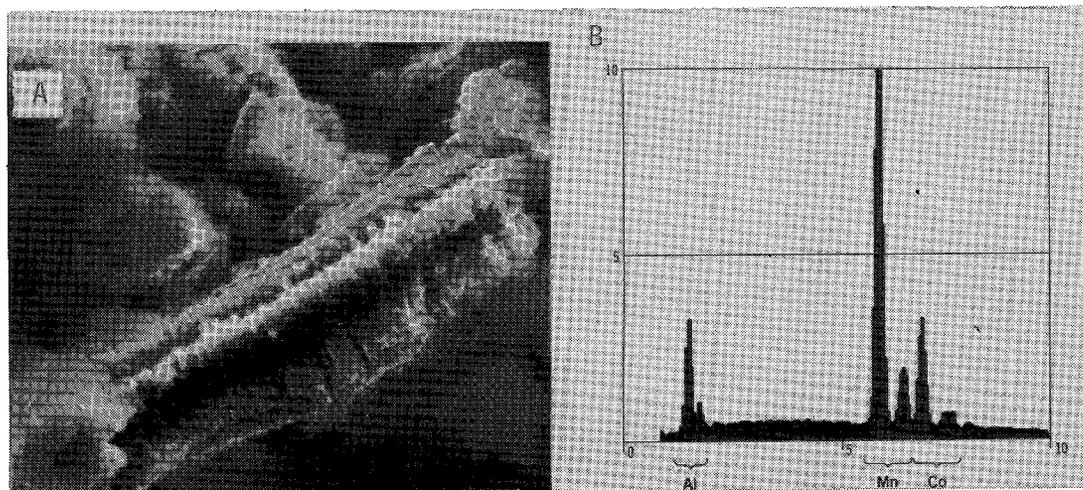


FIG. 6. (a) SEM photograph of lithiophorite crystals (2000x). (b) EDAX scan of lithiophorite crystal showing Mn, Al and Co peaks.

tion. The manganese oxides and iron oxyhydroxides appear to have formed at distinctly different times and in different hydrological environments. (2) Aller & Yingst (1978, p. 247) demonstrated that the innermost linings of polychaete burrows in Barnstable Harbor, Massachusetts, become "...enriched to a small extent in Fe and Mn oxides which accumulate by diffusion from the more reduced portions of the burrow wall..." In the burrow lining, these oxides act as scavengers of barium, cobalt, zinc, copper and other metals, as has been shown in various aqueous environments, *e.g.*,

in bogs in Sweden (Ljunggren 1955), in arid environments like desert surfaces (Engel & Sharp 1958) and in dendrites (Potter & Rossman 1978). Aller & Yingst (1978) postulated, moreover, that these metals tend to concentrate through time in the burrow lining as it thickens. The burrows they studied contain oxide inner layers surrounded by older Fe and Mn sulfide outer layers. The burrows found in this study probably were formed either in an environment similar to that Barnstable Harbor or in a more open marine environment, and the burrows were also probably loci for accumulation of manga-

nese oxide and associated metals. (3) A post-depositional weathering environment would not be favorable for barium adsorption by manganese oxide. Solutions involved in near-surface weathering generally are acidic. At pH less than 7, barium adsorption by manganese oxide is weak (Hem 1964). A marine environment at a pH of about 7.5 would provide more favorable conditions for the uptake of barium and other metals by manganese oxides.

These lines of evidence all support the hypothesis of a marine origin for the manganese oxide minerals in the burrow cement. The process of crystallization of hollandite and lithiophorite may have postdated burial of the burrows.

#### CONCLUSIONS

This and other occurrences of hollandite and lithiophorite indicate that these minerals can form in a variety of surficial or sedimentary environments. This occurrence also indicates that burrows have been sites of manganese oxide and trace-metal accumulation in past sedimentary environments. As shown by Aller & Yingst (1978), burrowing organisms can have a profound effect on the distribution of elements at the sediment-water interface.

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